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(54) SOFTENING COMPOSITIONS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E/C 4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns a fabric-softening composition. More particularly the present invention relates to a composition for reducing the rate of which cotton-containing fabrics become harsh or reducing the harshness of such fabrics, said composition comprising cellulolytic enzymes.

It is well known in the art that washing of fabrics can cause severe harshening of the fabrics. The degree of harshening is dependent upon a number of factors and conditions during washing operations, such as the detergent compositions used, the time and temperature of the washing operation, type of washing machine, the cloth/liquor ratio and the number of washes. This problem is particularly acute with fabrics made from cotton fibres, such as towels and napkins. Harshening of fabrics of this type has been recognized in the art, and several proposals have been made to reduce such harshening. They include treatment of the fibres after washing with a softening composition, which contains a cationic detergent as the effective agent. Such compositions also often referred to as rinse conditioners since they are normally applied in the rinsing stage of the washing operation, can have a satisfactory effect. A disadvantage of this method of alleviation of harshness of fabrics is, however, that it is only temporary, that is until the next wash, where the softening effect of the rinse conditioner is reduced.

It has been found that treatment with cellulolytic enzymes containing C_1 and C_x cellulases significantly reduces the rate at which new cotton articles become harsh and can partially restore the original softness to already harsh cotton articles. Cotton fabrics thus treated feel markedly softer after several washes than those treated with a conventional rinse conditioner. Surprisingly, furthermore, no significant fabric damage occurs under user's conditions of the compositions of the invention, although one would expect the cellulolytic enzymes to reduce the strength of the cotton fibres.

The present invention therefore provides a composition for reducing the harshness of cotton-containing fabrics, said composition comprising a cellulolytic enzyme as herein defined, and a detergent active material. Cellulolytic enzymes are well known; they are produced by fungi, for example by a submerged culture of a strain of Trichoderma on wheat bran. Other examples are fungal cellulolytic enzymes produced by cultures of Myrothecium verrucaria, Aspergillus orycae, Aspergillus niger, Botrytis cinerea. Bacterial cellulolytic enzymes are also known, e.g. produced by strains of Streptomycetes and Hymenomycetes. The cellulolytic enzymes to be used in the present invention contain two types of constituents, called Cellulase C_1 and Cellulase C_x, in which C_x is capable of splitting the β-glucosidic 1,4 bond of cellulose whereas the cellulase C_1 is not capable of doing so, C_1-cellulase is required for initial breakdown of cellulose. For further details, reference is hereby made to "Cellulases and their application", Proceedings of a symposium. American Society Special Publication 95 (1969) page 23. In this reference C_1-cellulase is defined as an enzyme whose action is unspecified. It is required for the hydrolysis of highly oriented solid cellulose by β-1,4 glucanases. The cellulolytic enzymes of the present invention may furthermore, in addition to C_1 and C_x cellulase contain minor amounts of other enzymes, such as cellobiase, xylanase, amylase, glucanase, protopectinase, maltase, saccharose, protease, lipase, pertinase and phospholipase.

Commercial C_1 and C_x cellulase-containing cellulolytic enzymes normally contain minor amounts of such other enzymes.

Cellulolytic enzymes are commercially avail-

e.g. Aspergillus, or from the pancreas; amylases such as those obtained by submerged fermentation of a particular strain of Bac. subtilis (commercially available from Royal Fermentation Industries, Delft, Holland, under the trade name Maxamyl® and from NOVO Industri A/S, Copenhagen, Denmark, under the trade name NOVO-amylase), and proteases, such as papain, trypsin, bacterial proteases of the subtilisin type, e.g. from Bac. subtilis, commercially available e.g., Alcalase® (ex NOVO) and Maxatase® (ex Royal Fermentation Industries), and Rhozyme J—25 (ex Rohm and Haas Cy), a powder mixture of a proteolytic enzyme and a minor amount of diastase, precipitated on corn starch as the carrier material for the enzymes.

The amount of cellulolytic enzymes to be used is of course dependent upon a number of factors, such as, in particular, their activity, duration of the fabric treatment, temperature and so on. For most practical purposes the amount of Meicelase P may lie between 0.01—20% by weight of the fabric-treating composition. The equivalent amount, in respect of C_1 activity, of another cellulolytic enzyme preparation may also be used.

The cellulolytic enzymes may be applied to the fabrics in the form of an aqueous solution, adjusted to the desired pH, or they may be formulated as a detergent active material-containing composition to be added to a wash liquor. Such a composition may be a (pre-) soaking composition, or a main wash composition or a rinse composition. It is preferred to apply fungal cellulolytic enzymes during (pre-) soaking, since the normal main wash compositions have a pH unsuitable for the incorporation of fungal cellulolytic enzymes. Since, furthermore, rinse compositions are normally acid, the cellulolytic enzymes with a pH optimum in the acid range can be used advantageously in such rinse compositions too.

It has been found that optimum results can be obtained with a combination of cellulolytic enzymes in a pre-wash step, and any suitable known rinse conditioning composition in the rinse step after the main wash. Often the results thus obtained are superior to either treatment alone.

The compositions of the invention may be in any suitable physical form, such as liquids, tablets, powders, noodles, and ribbons.

The compositions of the invention may comprise other constituents that are desirable in such softening compositions. Normally, a buffer system should be present if cellulolytic enzymes with an acid pH optimum are used in the compositions. In such a case, the minimum quantity of buffer should be used, in order to avoid as much as possible a drop in pH value of the main wash liquor due to the overflow of the (acid) pre-soak liquor to the alkaline main wash liquor. Too great a drop in pH value would impair the detergency of the main wash liquor. Citric acid, or any other suitable buffer system, proved to be satisfactory. More citric acid, with some sodium citrate, may also be used. Other suitable buffer systems are fumaric or benzoic acid.

The compositions furthermore contain a detergent active material. Although it has been suggested that anionic detergent active materials inhibit cellulolytic enzymes, tests have been carried out to this effect, and some anionic detergent active materials like sodium dodecylbenzenesulfonate proved to be strongly inhibitory to the cellulolytic enzymes. Others, like fatty alcohol sulphates proved to be less inhibitory, and alkyl ether sulphates and -carboxylates proved to give almost no inhibition. The inhibition can be reduced by incorporation of nonionic detergents. Nonionic detergent active materials did not seem to be significantly inhibitory, nor did tertiary amine oxides or sulpho-betaines, and cationic detergent active materials are said in the prior art not to inhibit the cellulolytic enzymes at all. The compositions of the invention therefore preferably contain a nonionic and/or a cationic detergent active material. Suitable examples of anionic, nonionic and cationic detergent active material can be found in Schwartz, Perry and Berch "Synthetic Detergents and Surfactants", Vol. II, 1958. Furthermore, fillers such as sodium sulphate, perfumes, germicides, hydrotropes, opacifiers, solvents, fluorescers, foam-depressors, stabilizing agents for liquids and colouring material may also be present. The cellulolytic enzymes may also be incorporated in normal rinse-conditioning products of which examples are described in Chemistry and Industry, July 1969, page 903.

Example 1.

The following comparative test was carried out. An aqueous buffer solution with pH 5 was prepared from 10.6 g citric acid monohydrate and 18.3 g monosodium dihydrogen orthophosphate $2H_2O$. 5 g pieces of an extremely harsh cotton terry towelling (cloth A) were soaked for a weekend in 200 ml portions of the aqueous solution at 30°C in the presence of additive as given below.

	Treatment	Towel No. 1 Breaking strain in Kg		Towel No. 2 Breaking strain in Kg	
A	1 × washing with normal heavy-duty detergent composition[2])	35.6 35.2 37.8	30.8	34.4 35.8 33.2	34.5
B	1 × washing with normal heavy-duty detergent composition[2]) + 12 further washes in water (cloth B)	33.3		18[x]	
C	Cloth B again washed and treated with cellulase in pre-wash cycle of washing machine	32.9 32.4 29.4	31.8	32.4 32.0 31.4	31.9
C[1]	Cloth B again washed but without cellulase in the prewash cycle of washing machine.	33.8 30.3 33.3	32.5	34.8 35.4 26.8	31.8

[x]probably due to unknown malfunctioning of machine during test.

These tests indicated that the loss in strength one would expect accompanying the cellulase treatment was either small or zero. In an additional test, 55 g cotton (13 times washed) was treated for 1 hour at 50°C in the washing machine with 2.7 g cellulase, buffered at pH 5. No reduction in the degree of polymerization of cotton could be found.

Example 6.

Example 4 was repeated (temperature 50°C, soaking time 18 hours: pH 5, drying at 20°C/65% R.H.) with 0.08 g cellulase ex Merck (activity 20 mU/mg), 3.4 g cellulase C 7377 ex Sigma or 3.4 g cellulase 36 concentrated ex Rohm and Haas. The same softening as with 0.2 g Meicelase P was obtained.

Example 7.

The test articles were four cotton towels that had been harshened by 14 washes in a drum-type washing machine. Two of the towels were treated at 20°C with a conventional rinse conditioner[1]) in aqueous solution for 10 minutes. The liquor to cloth ratio was 7:1 and the cloth to rinse conditioner ratio was 70:1. After line drying these articles (A) were substantially softer than the two articles (B) which had not been treated with the conventional rinse conditioner.

The test proceeded as follows in the drum-type washing machine:

Article	Meicelase P	Conventional rinse conditioner [1]
A	—	—
B	—	42 g
C	20 g	42 g
D	20 g	—

The conditions were as follows:

weight of test articles	325 g
weight of ballast articles	3 kg
buffer solution (pH = 5)	51.5 g citric acid monohydrate + 91.5 g $Na_2HPO_4.2H_2O$
duration/temperature	15 min to 50°C. then 45 min at 50°C.

At the end of the treatment the articles were removed from the machine and dried on a line. The four pairs of articles were ranked by three observers in order of increasing softness, with 1 being assigned to the harshest cloth and 4 being assigned to the softest cloth in each of the two series.

Results:

Cloth	Rank totals
A	6
B	9
C	22
D	19

It was concluded that the enzyme was effective for softening and that the combination enzyme/conventional rinse conditioner was apparently superior to either alone.

Example 9.

Cotton towels harshened by 10 washes in a drum-type washing machine were used.

These articles were then treated in the washing machine with the following products:

Article	Pre-wash	Main wash		Rinse
I	Buffer, pH 5 (citrate/phosphate) 15 g conventional rinse product [1] 2 g Meicelase P volume of solution 18l	130 g	conventional heavy-duty detergent composition [2]	(a) — (b) 42 g conventional rise product [1]
II	Buffer, pH 5 (citrate phosphate) 15 g conventional rinse product [1] volume of solution 18l	130 g	conventional heavy-duty detergent composition [2]	(a) — (b) 42 g conventional rinse product [1]
III	Buffer (pH 5 using citrate/phosphate) volume of solution 18l	130 g	conventional heavy-duty detergent composition [2]	42 g conventional rinse product [1]

main wash product, and rinse product, as indicated below. When a rinse product was used it was added at the beginning of the last rinse. At the end of each washing cycle the towels W and G were dried on a line. 14 repeat cycles were carried out.

Pre-wash	Main wash	Rinse	softness ratings	
			W	G
conventional heavy-duty detergent composition[2])	conventional heavy-duty detergent composition [2])	—	0	−2
conventional heavy-duty detergent composition [2])	conventional heavy-duty detergent composition [2])	conventional rinse conditioner [1]) x	3	3
buffer (pH of 5) volume of solution 22l containing 51.5 g citric acid 91.6g $NaH_2PO_4 2H_2O$	conventional heavy-duty detergent composition [2])	—	2	2
buffer + 2 g enzyme (as above) (as above)	conventional heavy-duty detergent composition [2])	—	5	5
buffer + 20 g enzyme (as above (as above)	conventional heavy-duty detergent composition [2])	—	8	6
buffer + 2 g enzyme (as above) (as above)	conventional heavy-duty detergent composition [2])	conventional rinse conditioner [1]) x	10	7

xonly 1/1.7 of the recommended concentration was used (i.e. 25 g in the rinse)

rating: 1 = feel of the 25 times washed cloth (harsh) 10 = feel of the once washed cloth (soft)

Example 13.

In a drum-type washing machine, using its normal programme, 3 kg dirty wash goods and harsh cotton towels which had been washed 14 times were laundered.

In experiment A, a pre-wash product was used of the following composition:

80 g sodium sulphate
20 g Meicelase P
10 g sec. C_{11-15} alcohol condensed with 9 moles of ethylene oxide
20 g benzoic acid.

The pH at the end of pre-wash was 4.9. The solution volume was 22 l. In the main wash 180 g of the conventional heavy-duty detergent composition[2]) was used. The pH at the end of the main wash was 9.4. The wash goods and towel were rinsed with tap water and dried on a line. In experiment B, the pre-wash was carried out with 60 g of the conventional heavy-duty detergent composition[2]) (pH at the end of the pre-wash was 9.4) and the main wash with 150 g of the same product (end pH 9.6).

The rinse was carried out in the normal rinse cycle with tap water and the wash good and towel were dried on a line.

The towel in Experiment A felt noticeably softer after washing than in Experiment B.

WHAT WE CLAIM IS:—

1. Method for reducing the rate at which cotton-containing fabrics become harsh or reducing the harshness of such fabrics comprising applying cellulolytic enzymes as herein before defined to the fabrics.

2. Method according to Claim 1, wherein the cellulolytic enzymes are applied in a soaking process.